Environment Canada
Conservation and Protection

Environnement Canada
Conservation et Protection

SEDIMENTS IN WATER QUALITY ASSESSMENTS: OPPORTUNITIES FOR INTEGRATING WATER QUALITY AND WATER RESOURCES BRANCHES' ACTIVITIES

D. P. BLACHFORD AND T. J. DAY

Canada

SEDIMENT SURVEY SECTION
IWD-HQ-WRB-SS-88-2

88-06167/

0420D

SEDIMENTS IN WATER QUALITY ASSESSMENTS: OPPORTUNITIES FOR INTEGRATING WATER QUALITY AND WATER RESOURCE BRANCHES' ACTIVITIES

IWD-HQ-WRB-SS-88-2

D.P. Blachford and
T.J. Day
Sediment Survey Section
Water Resources Branch
Inland Water Directorate
Environment Canada
Ottawa, Ontario
K1A 0H3

EXECUTIVE SUMMARY

The Inland Waters Directorate has opportunities for integration of operational activities in addressing the issue of the role of fluvial sediments in environmental quality. These sediments, particular their fine proportions, play a dominant role in the quality of the aquatic environment as they are capable of transporting quantities of nutrients and contaminants to and within aquatic systems, and of regulating nutrient and contaminant availability to the biological community.

Determining the status of aquatic quality is the primary responsibility of Water Quality Branch. Water quality assessments conducted by the Branch provide data and information regarding aquatic quality. The goals of the assessments are to establish baseline conditions and long term trends, to provide data for environmental impact assessments and to monitor for the development of or compliance with water quality objectives. The Sediment Survey Program of Water Resources Branch provides data on particle size and sediment concentration as well as information on seasonal and spatial variability of suspended sediment in fluvial and lacustrine systems. The goals of the assessments can only be met with the availability of this type of physical sediment data.

The roles of Water Quality and Water Resources Branches can be linked with regard to the procurement and usage of sediment data as part of water quality assessments. Water Resources Branch through its Sediment Survey activities provides expert advice on sediment dynamics, interpretation and physical description of sediment. Water Quality Branch provides advice on ecosystem dynamics, pathways that include sediments, environmental processes and interpretation. A unique and important opportunity exists through inter-Branch co-operation to address sediment issues be they toxic-related or simply a physical characteristic capable of limiting bioproductivity.

This report identifies opportunities for a new and improved working relationship between the Branches.

RESUME

La Direction générale des eaux intérieures bénéficie d'occasions d'intégrer ses activités opérationnelles lorsqu'elle s'occupe de la question du rôle que jouent les sédiments fluviaux dans la qualité de l'environnement. Ces sédiments, notamment en raison de leurs petites dimensions, exercent une influence notable sur la qualité du milieu aquatique, car ils peuvent transporter des éléments nutritifs et des contaminants vers les systèmes aquatiques et à l'intérieur de ceux-ci ainsi que contrôler la quantité de ces substances qui atteignent la communauté biologique.

La Direction de la qualité des eaux a comme responsabilité première de déterminer la qualité de l'eau. Elle effectue pour ce faire des évaluations de la qualité des eaux afin de recueillir des données et des informations concernant la qualité du milieu aquatique. Ces évaluations visent à déterminer les conditions de base et les tendances à long terme, à fournir des données devant servir aux évaluations des incidences environnementales et à contrôler l'élaboration d'objectifs de qualité des eaux ainsi que le respect de ces objectifs. Dans le cadre de son programme d'étude des sédiments, la Direction des ressources en eau fournit des données sur la granulométrie et la concentration des sédiments de même que des renseignements sur la variabilité des sédiments en suspension dans les cours d'eau et les lacs selon les saisons et dans l'espace. Ce type de données sur les sédiments est essentiel pour satisfaire aux buts de telles évaluations.

Un lien peut être établi entre les rôles que jouent la Direction de la qualité des eaux et celle des ressources en eau en ce qui concerne l'obtention et l'utilisation des données sur les sédiments dans le cadre des évaluations de la qualité des eaux. Grâce à ses activités en matière d'étude des sédiments, la Direction des ressources en eau prodigue des conseils sur la dynamique, l'interprétation et la description physique des sédiments. Pour sa part, la Direction de la qualité des eaux donne des conseils sur la dynamique des écosystèmes, les cheminements dont les sédiments, les processus environnementaux et l'interprétation. Le développement d'une collaboration entre les Directions constituent une occasion sans pareil de s'attaquer aux problèmes relatifs aux sédiments qu'il s'agisse d'une question de toxicité ou seulement une caractéristique physique capable de limiter la productivité.

Le présent rapport présente des façons d'améliorer les relations de travail entre les Directions.

ACKNOWLEDGEMENTS

The authors wish to thank the Sediment Survey Section of Water Resources Branch for providing much of the resources and the opportunity to prepare this report. Throughout the preparation of the report input and reviews have been received from many people. Particular thanks is due to G.D. Haffner, W.B. Gummer, E.D. Ongley, and T.R. Yuzyk.

CONTENTS

	Page
EXECUTIVE SUMMARY	i
RESUME	ii
ACKNOWLEDGEMENTS	iii
CONTENTS	iv
TABLES	v
1. INTRODUCTION	1
1.1 Purpose of Report	1
1.2 Scope of Report	1
1.3 Objectives of Report	2
2. SEDIMENT - WATER QUALITY ISSUES	3
2.1 Introduction	3
2.2 Identifiers of Contaminant Presence	6
2.3 Contaminant Transport and Fate	7
2.4 Regulators of Contaminant Partitioning	9
3. INFORMATION AND DATA NEEDS FOR WATER QUALITY ASSESSMENTS	11
3.1 Introduction	11
3.2 Information Requirements	11
3.3 Data Requirements	15
4. OPPORTUNITIES FOR OPERATIONAL PROGRAMS	20
4.1 Present Status of Sediment Activities	20
4.1.1 Water Quality Branch	20
4.1.2 Water Resources Branch	21
4.2 Recommended Improvements for Efficiencies and Effectiveness in Sediment Activities	22
5. FUTURE CONSIDERATIONS	29
6. REFERENCES	31
APPENDIX I Sediments and Water Quality: Background Scientific Information	
APPENDIX II Analytical Methods and Measurements	

TABLES

Page

Table 1. Incorporation of Sediment into Water Quality Assessments 12

Table 2. Sediment Information Needed for Sampling Design 13

1. INTRODUCTION

1.1 Purpose of Report

This report is directed at managers in the two operational Branches of Inland Waters Directorate, and is intended to inform them of the opportunities for joint work on the physical and chemical aspects relating to the source, transfer and fate of sediments and the materials that move with them in inland waters.

The report has been prompted by the shifting of the Sediment Survey activities of Water Resources Branch towards a better balance between strictly data collection and addressing issues, which are predominantly ones of environmental quality, and by the recognition in the Water Quality Branch that comprehensive assessments of the quality of the aquatic environment require sediment data and information, as well as expertise and advice on sediment process.

1.2 Scope of Report

The report begins with an evaluation of the importance of sediments in water quality assessments and identifies data and information requirements. The present capability of the two Branches to provide the required expertise, data and information is assessed, the opportunities for joint work identified and recommendations for cooperation are formulated. The report ends with statements on research needs.

Also, two appendices, one on background scientific information and the other on analytical methods and measurements, are provided for those Branch staff who want to pursue more specific aspects.

1.3 Objectives of the Report

It is appropriate at this time to investigate mechanisms by which Water Quality Branch and Water Resources Branch can work together in order to ensure scientifically sound implementation of water quality assessments and to fulfill client demands for sediment data. To this end, this report is jointly prepared by the two Branches.

The objectives of the report are:

1) to inform Inland Waters Directorate managers about sediment-water quality relationships;
2) to discuss sediment-water quality issues;
3) to establish the relative importance of sediments in aquatic quality assessments;
4) to document the type of sediment information required by water quality assessments; and
5) to investigate methods of coordinating activities carried out by IWD to improve the effectiveness of current and future programs.

2. SEDIMENT - WATER QUALITY ISSUES

2.1 Introduction

Current sediment issues in Canada fall into two broad categories - those that relate to the physical presence of the sediment itself and those related to the chemicals it carries. Traditional work carried out in the Sediment Survey Program has focussed upon the former issues: information has been collected for concerns such as reservoir sedimentation, basin sediment yields, effects of engineering works and land use changes and erosion. Increased attention in Canada, however, is being devoted to the chemical aspects of sediment.

Sediment chemistry has gained recognition over recent years as the concern for contaminants in the aquatic environment developed and, concurrently, it became common knowledge that many contaminants associate with sediments. Issues concerning aquatic quality relate to the role of sediments as sinks and sources of toxics and nutrients, and as transporters of pollutants. Linked to these issues are questions concerning the origin of the sediments and the contaminants, the fate of the sediment-contaminant assembly and the potential environmental effects of the sediments and contaminants.

A recent inquiry of sediment data users across Canada, carried out under contract for the Sediment Survey Section, highlights the need

for information on sediment quality issues. For example, almost 30% of sediment data users in Ontario require data for water quality purposes. About 40% of data users require data for sedimentation studies; however, these studies involve more applications to sediment quality than quantity. The data users are concerned with sediment sources, what contaminants are associated with sediments and where sediment deposits are potential sinks/sources of contamination (Conservation Management Systems, 1985).

There is a demonstrated need for sediment quality data in Quebec (Hydrotech Inc., 1985) where the identification and tracking of contaminants in the St. Lawrence River, as well as in other areas, has been successfully carried out. Other uses of sediment quality data in Quebec are for studies of the environmental impacts of agriculture and forestry. Sediment data requirements in British Columbia (Kellerhals Engineering Services Ltd., 1985) include data largely for engineering purposes (navigation, dredging), although sediment quality concerns (sediment sources and delivery, sediment as a transporter of pollutants, effects of source development, effects on fisheries) were also expressed.

In the Prairie Provinces, water resources engineering and land use and management issues were identified, along with considerable interest in sediments as a physical issue in water bodies and as a transporter and source of undesirable substances (Northwest Hydraulic Consultants, 1985). Sediment data needs in the Atlantic provinces are

oriented towards activities which may affect water quality and the aquatic environment (Washburn & Gillies Assoc. Ltd., 1985).

Clearly, there is a need for data on sediment quality and for an understanding of its role in determining water quality conditions. Collection of sediment quality data is essential for conducting sound water quality assessments. There is presently very limited collection of sediment quality information. Relatively less is known about how, where and when to sample for sediment quality than for sediment quantity or for the quality of the water media. In this chapter the following are presented in relation to the sediment roles in water quality assessments: a discussion of the various sediment quality issues and how the issues can be addressed by the objectives of the assessment program. The roles of sediment, as stated earlier, are:

1) identifiers of contaminant presence;
2) contaminant transport and fate; and
3) regulators of contaminant partitioning between the aqueous and biological compartments.

In this report, the term "contaminant" means any substance deemed to be undesireable (e.g., toxic chemicals, nutrients). Further information on the role of sediment, as summarized in this chapter, are presented in Appendix I.

2.2 Identifiers of Contaminant Presence

The roles that sediments play in the evaluation of water quality are due to the tendency of substances (particularly contaminants such as organics and metals with low solubilities in water) to adsorb to the surface of particulate matter in the water column. The tendency of contaminants to associate with particulates increases as the size of the particles decreases, and as the proportion of organic to inorganic matter increases. Kuntz and Wary (1983), for example, found the concentrations of organochlorine contaminants associated with sediments in the Niagara River were 400 to 500 000 times greater than in the aqueous phase. Because of the contaminant partitioning to sediment, contaminants which are present in undetectable amounts in water may be readily identified in sediments. The sediment concentration and the amount of fine-grained material determine the relative importance of the sediment and aqueous compartments.

It is well known that Canadian waters are impacted by pesticide runoff and spray from agricultural lands and forestry, by toxic chemicals from industrial effluents and storage sites and from urban areas. Water Quality Branch, Inland Waters Directorate, monitors for contaminants in water collected from across Canada, and yet detectable levels of the substances are rarely observed. In the prairies, for example, 94% of pesticide and herbicide analyses in water (n=83162) were below the detection limits. Collection of sediment samples for analysis of

contaminants, and of supporting sediment size, organic content and concentration data, can enable identification of contaminant presence and trends, tracing of contaminant movement in fluvial systems, estimation of areas and magnitude of potential effects, and will provide a data base from which to develop and monitor for compliance with water quality objectives.

2.3 Contaminant Transport and Fate

The transport path and final region of deposition of sediment-related contaminants are determined in part by the sediment regime. Knowledge of the contaminant presence and sediment dynamics can help delineate zones of source and impact. Thomas (1983), for example, studied the distribution of PCBs, mercury and mirex in Lake Ontario and was clearly able to identify sources of the contaminants and to observe the influence of sediment transport on contaminant fate.

A clear understanding of the sediment dynamics (source, transport and fate) of specific systems is essential for designing physical sediment and water quality collection strategies and for interpretation of the resulting data. Apart from characteristics of the substance itself, the major factors which affect sediment-contaminant concentrations, such as particle size, organic content and sediment concentration are seasonally controlled by the discharge regime and by local, short-term events. The presence of contaminants in the aquatic medium may or may not be seasonal and discharge-related, depending upon

point and diffuse sources of the substance, land use practices, etc. For example, metals from a point source may be observed at relatively low concentrations in spring, due to dilution by high flows and high sediment concentrations, and at relatively high concentrations in summer and fall, when sediment organic content peaks and sediment concentration is at a minimum causing a greater impact of contaminant per unit weight of sediment. Open-water metal loadings, however, are dominated by the high spring sediment loads. Major transport of PCB in the Hudson River has been observed during spring run-off and storm events, when suspended sediment concentrations were high, whereas organic contaminant transport in the James River was observed to peak during the summer when biological productivity increased and with it partitioning to suspended organic colloids.

The source of the contaminants and the physical and chemical characteristics of the water body at the time of contaminant introduction determine the bioavailability and thus the ultimate fate of contaminants. Metals, for example, may be part of the sediment particle itself and therefore not be available to aquatic biota under natural conditions. On the other hand, contaminants may become attached to mineral and/or organic matter coatings on sediment particles and be released under certain conditions immediately, be transported and released (and made bioavailable) in locations far from the site of introduction of the contaminant, or may ultimately be buried with the sediment and cause no adverse environmental effects. The ever-changing conditions governing the

sediment-contaminant attachment and the movement of the sediment itself are responsible for the location and potential aquatic effects of sediment-related contaminants. Study of sediment transport and fate will provide a data base for environmental impact assessments and to facilitate interpretation of baseline and long term trend data.

2.4 Regulators of Contaminant Partitioning

Sediments and contaminants in the water medium are at a continuous disequilibrium. Some contaminants are actively removed by sediments from the water column due to their low solubility and tendency to shift from the solute to solid phase. A variety of processes counter-balance this and cause the release of contaminants from the sediments. Concentration of contaminants on sediments may have favourable effects by diminishing the concentration in the soluble phase, or it may lead to adverse effects due to, for example, ingestion of contaminant-rich sediment by biota.

Physical, chemical and biological processes release and recycle sediment-related contaminants. Resuspension of bed sediments in lakes occurs by wave and current action, while remobilization of sediment in rivers is dominated by the discharge regime. These processes re-introduce sediment-contaminants to the aquatic ecosystem from a previously inactive state. Chemical factors, such as increases in salinity and decreases in pH, may cause replacement and dissolution

respectively of substances attached to sediments. Bioturbation of bottom sediments and microbial activity, such as methylation of mercury, are biological processes which similarly re-introduce contaminants to the aqueous phase. An understanding of these processes, and their role in controlling the relative amounts of contaminant in the aqueous and solid phases, is essential for estimating bioavailability and therefore for the development of water quality objectives and for environmental impact assessment.

3. INFORMATION AND DATA NEEDS FOR WATER QUALITY ASSESSMENTS

3.1 Introduction

The relationship between the roles of sediment, the goals of water quality assessments and the data and information requirements are shown in Table 1.

The table expresses the physical sediment data and information required for water quality activities. Some of the data are needed for the planning of sediment quality sampling strategies (such as particle size distribution in a cross-section/reach, seasonal sediment concentrations), while other data must be collected at the time of sediment collection for contaminant analysis.

3.2 Information Requirements

Physical and chemical sediment data must be collected by strategies that generate the information needed for addressing the goals of the assessments. Some data may be collected at fixed sites at defined time intervals. Other types of data or information necessitate a more flexible sediment collection approach with sites and frequencies determined by the purpose of the activity. Whereas sample collection for sediment quality issues differs for the two approaches, similar knowledge of sediment regime is required. Sediment information needed for designing a sampling strategy is presented in Table 2.

Table 1. Incorporation of Sediment into Water Quality Assessments

Sediment Role	Goals of the Assessments	Data & Information Requirements
1. Identify contaminant presence	Establish baseline conditions and long term trends	Particle size, organic content, sediment concentration information (at site and in basins) on seasonal and spatial variability of suspended sediment, concentration of contaminant.
2. Contaminant transport and fate	Provide data for environmental impact assessments	Particle size, organic content, sediment concentration information (at site and in basins) on seasonal and spatial variability of suspended and bottom sediments, concentration of contaminant.
3. Regulation of partitioning (aqueous-biological)	Monitor for development of or compliance with water quality objectives Provide data for environmental impact assessments	Particle size, organic content, sediment concentration information (at sites and in basins) on seasonal and spatial variability of suspended and bottom sediments. Research on physical, chemical, biological interactions.

Sediment information for establishing baseline conditions and long term trends can largely be generated from fixed site sampling. Routine reporting of particle size and sediment concentration is needed to establish an initial understanding of the sediment regime in each system. Continuation of routine sampling after an appropriate data base is established will depend upon data variability; examination of the data

Table 2. Sediment Information Needed for Sampling Design

		Required Information	Use of Information
Spatial	a)	site - cross-sectional variations in particle size sediment concentration	micro-site selection
	b)	basin - downstream variations in particle size sediment concentration	site selection
		- tributary effects - locations of erosion deposition	
Seasonal	-	variability with discharge over the hydrologic year and between years of particle size sediment concentration organic carbon content	sampling frequency
	-	variability of sediment sources	sampling frequency

may reveal that spot checks (non-routine sampling) would be adequate for future data collection. The suitability of sites for collection of sediment for contaminant analysis, and the possibility of extrapolating sediment data collected at one site/reach to another, must be investigated. Collection of sediment for contaminant analyses must include considerations of sediment regime as well as contaminant characteristics. Knowledge of the physical sediment is needed for sediment sampling (for chemical analyses), and for interpretation of the sediment-related data.

Information for environmental impact assessment and for development and monitoring for compliance of water quality objectives must be generated primarily from creative, non-routine activities with supporting information coming from fixed site sampling. The creative studies would be carried out in a specified basin or section of a basin. Due to the exploratory nature of issues addressed by studies, it is unlikely that the necessary background water quality and sediment data would exist in the region or at the scale required. This could be provided by a time-limited, intensive study designed to characterize water chemistry and sediment characteristics. The physical sediment part of the study would be similar to sediment studies that are not related to water quality issues i.e., investigation of sediment sources, transport and fate. The water quality studies would focus on multi-media sampling for impact assessment as well as a large research component for the development of objectives.

3.3 Data Requirements

The following physical sediment data are required to meet the goals of water quality assessments:

1) particle size
2) organic content
3) suspended sediment concentration
4) concentration of parameter of concern and supporting data.
5) mineral type
6) surface characteristics.

It must be emphasized again that while some of the physical sediment data are needed for characterization of each system, the physical data must also be collected in conjunction with sediment collection for chemical analyses. Failure to do so would result in sediment chemistry data which could not be meaningfully interpreted. Data requirements must be carefully planned to avoid excessive collection.

Analytical methods and measurements are summarized in Appendix II.

1) Particle Size

The particle size distribution of sediment samples collected for sediment chemistry analyses must be determined. As sediments in the

silt/clay range are the greatest carriers of contaminansts such as metals and nutrients, the proportion of sediment by weight $\leq$ 62 um and > 62 um is essential for interpretation of the data. The grain size range with which organic compounds associate is uncertain; this should be determined so that the appropriate size fraction can be targeted for analysis.

The minimum sample weight required for particle size analysis is 0.15 g. Sediment for size analysis should be separated from the sample collected for sediment chemistry analyses.

2) Organic Content

The organic carbon content of sediments collected for chemical analyses must be determined. This will help resolve seasonal and site differences in contaminant concentration and may explain contaminant accumulation or dilution in a sediment sample. Although the exact relationship between organic carbon and contaminant levels is unclear, the fact that contaminants are preferentially associated with organic sediments make the proportion of organic carbon in a sediment sample useful during data interpretation.

The sample weight required for organic carbon analysis is 0.6 - 0.8 mg. Sample for the analysis should be separated from the sample collected for sediment chemistry analyses.

3) Suspended Sediment Concentration

The cross-sectional mean suspended sediment concentration, or a field-proven, representative value estimating the mean, is required for interpretation of sediment chemistry. This is essential for calculating total sediment-contaminant amounts within each reach and the total loading to a receiving water body. Potential impacts of the contaminant can then be estimated.

Data on sediment concentrations would be needed in advance of sediment chemistry sampling for temporal and site selection purposes. It would also need to be collected at the time of sediment chemistry sampling to aid in interpretation.

4) Concentration of Parameter of Concern and Supporting Data

Study of toxic contaminants requires, at a minimum, data on the total concentration of contaminant of concern associated with sediment (suspended and/or bottom). Auxilliary data required for interpretation of sediment-contaminant data depends upon the study purpose. Sediment data for long-term trends may be complimented by concentrations in biota. Data for impact assessment may require information on mineralogy and sediment storage areas and/or bioavailability estimates (e.g. specific information on the association of contaminants with sediment). Sediment collected for development of objectives would require, for example, data on oxygen concentration, pH levels, salinity and biological activity.

Sediment quantities required for analysis of the parameters of concern are varied. Approximate amounts of some contaminants are:

organochlorine pesticides and PCB's	10 g
oil and grease	10 g
mercury	5 g
heavy metals	0.1 g

The quantities, and the special handling requirements of samples for analysis of many of the parameters, deserve careful consideration when selecting equipment, personnel and designing strategies for sediment chemistry sampling. Failure to use correct equipment and methodology may produce uninterpretable results.

5) Mineral Type

Knowing the major mineral types represented in the sediment matrix will provide valuable insight into the chemistry of the system. As minerals are stable and react slowly this will be more important for long term assessments.

6) Surface Characteristics

It is now clear that surface reactions have a profound influence on sediment and water chemistry. It is not clear what those reactions are. An initial step would be to understand the nature and distribution of the surface characteristics. Evaluations can then be made of the

reaction potential of the site and an estimate made of the reaction mechanism. Those theories can be related to associated water chemistry and will eventually load to a better understanding of the role played by surface reactions in the sediment and water interactions.

It should be noted that the types of analysis required to obtain data for 5 and 6 are not presently done by the WQB or WRB.

4. OPPORTUNITIES FOR OPERATIONAL PROGRAMS

4.1 Present Status of Sediment Activities

4.1.1 Water Quality Branch

Water Quality Branch (WQB) is responsible for providing information on the status of aquatic quality. This involves information provision on national and regional water quality issues and systems management within river basins. Water quality assessments are designed to provide this information. Diverse components of the environment are monitored, as opposed to the traditional focus solely on the water medium. Focus in the planning of assessments is on physical and biological sampling to complement routine chemical monitoring.

The importance of sediment sampling in the resolution of contaminant issues has been emphasized by Chapman et. al. (1982). They evaluated the Environmental Protection Agency list of priority pollutants and recommended which environmental compartments should be sampled based on the anticipated fates and effects of the compounds. Sediment is the recommended sampling medium for 67% of these chemical compounds, biota for 50% and water for 34%. Understanding pollutant transport, fate and effects in aquatic systems clearly necessitates sediment sampling.

Current monitoring programs carried out by WQB, however, including those for sampling contaminants, are oriented towards water collection and analysis. Only 18% and 21% of Water Quality Branch activities in 1984-85 involved sediment and biological sampling respectively (WQB, 1986). This represents less than a quarter of the total expenditures on water quality activities. Given the priority of contaminants in the WQB program and the information potential of sediment chemistry data, there appears to be an increased need for sediment data by WQB.

4.1.2 Water Resources Branch

Water Resources Branch (WRB) is responsible for providing data and information on many aspects of sediment transport and fate in inland waters. The main effort traditionally has been directed towards collecting sediment transport data at hydrometric sites. The derived data are primarily of suspended sediment but other data on bed material and bedload are available for selected sites. Presently, such data are being collected at approximately 200 sites, with data existing for about 400 discontinued stations. As part of their overall sediment surveys activities Water Resources Branch also has participated in special field studies and surveys including extensive reservoir surveys.

As noted in Section 2.1 Water Resources Branch has recently completed a major evaluation of its sediment survey program. The main redirections resulting from their efforts are: a shift towards issues,

while still maintaining basic data collection; a shift from focussing solely upon water resource engineering applications to consideration of a full range of environmental (e.g. fisheries) and quality applications; and, a shift to shorter, less detailed data records.

The need to link the sediment survey program to the transport of sediment-associated contaminants is considered to be a main finding of this evaluation exercise and is being pursued through preparation of this report.

4.2 Recommended Improvements for Efficiencies and Effectiveness in Sediment Activities

Interaction between Water Quality Branch and Water Resources Branch is clearly needed for the efficient implementation of scientifically sound sediment quality activities. Incorporation of the sediment component into water quality assessments can take place at many program levels, discussed below.

Sediment information collection can be incorporated into water quality assessments as part of Water Quality Branch's index station and river basin survey approaches (WQB, 1986). The index stations, strategically located within key river basins, are sampled at regular intervals over the long term to provide baseline data on water quality conditions and an indication of changes and long-term trends. Basin surveys should provide information on the environmental significance of

water quality conditions. The surveys must be designed to understand the behaviour of the system (as opposed to conditions at a site), determine sources, pathways and impacts of specific parameters and identify existing or emerging water quality concerns. Information obtained from the index and survey networks may be augmented by special studies. These should be set up independently and designed to obtain comprehensive information on localized conditions (e.g., site representativeness) or national issues (e.g., impact of land use practices on water quality).

Regardless of the approach chosen for implementing sediment activities, interaction between Water Quality Branch and Water Resources Branch must take place regarding:

1) sampling design
2) sample collection
3) laboratory analyses
4) data storage and access
5) data publishing
6) data interpretation and
7) implementation

1) Sampling Design

The sediment-water quality activities must be designed jointly by WQB and WRB to ensure that sediments are collected in a scientifically

defensible manner that addresses the needs of the assessment program. The WQB should indicate for which river systems baseline physical sediment data are required. The WRB should provide advice on the suitability of WQB sites for sediment collection, and the possibility of establishing new sediment stations or of using data collected at existing sediment stations at WQB sites. WRB advice would also be required regarding appropriate sampling frequencies to meet the objectives of the sampling activities, interpretation of sediment regime, sampling locations in a reach and cross-section, etc. The research institutes could also be consulted at the project design stage on a need basis. It is the responsibility of WQB to state the type of sediment data that are needed and of the WRB to indicate the most effective way of obtaining the physical sediment data.

IT IS RECOMMENDED THAT WQB AND WRB - IN CONJUNCTION WITH RESEARCHERS WHERE APPROPRIATE - JOINTLY PLAN AND DESIGN SEDIMENT COLLECTIONS.

2) Sample Collection

Sediment sample collection for developing an understanding of sediment regime should be undertaken by WRB. Sample collection for physical data coinciding with collection for chemical purposes must be closely coordinated with WQB. Sampling equipment and procedures should be evaluated by both branches, with developmental participation of the research institutes.

IT IS RECOMMENDED THAT WRB AND WQB CO-ORDINATE THE COLLECTION OF PHYSICAL AND CHEMICAL SEDIMENT DATA TO THE EXTENT FEASIBLE.

3) Laboratory Analyses

It has been recommended that samples for particle size and organic content analyses be separated from sediment samples collected for chemical analysis. WQB labs have the capability for organic carbon analysis and WRB labs for particle size analysis. Specific concerns include, for example, the number of samples requiring organic carbon and particle size analysis to characterize the hydrologic year. Discussions between WQB and WRB staff will be needed to establish sample delivery, quality control, etc. Over the longer term, however, it could be more cost-effective, efficient and insure higher quality data to amalgamate lab facilities. This should be investigated by the Branches.

IT IS RECOMMENDED THAT INTEGRATION OF PHYSICAL AND CHEMICAL ANALYTICAL FACILITIES BE INVESTIGATED.

4) Data Storage and Access

The recent availability of so-called "4th generation" computer languages will solve many of the access problems which prevailed in the past. Software such as ORACLE will allow efficient access and manipulation of data from either data base for a range of uses.

IT IS RECOMMENDED THAT EACH BRANCH SHOULD PURSUE HARMONIZATION OF SOFTWARE.

5) Data Publishing

Both WQB and WRB presently publish a range of data and technical reports based upon these data. However, presently there is little cross-reference between these publishing efforts. Many users of sediment or water quality data will need data or at least need to know of other existing pertinent data. There are several ways of publishing the data including: add organic carbon data to the annual sediment publications and leave WQB regional data publications "as is"; incorporate particle size, organic carbon and sediment concentration data into the WQB detailed publications; publish basin reports on an annual basis, with all the available water resources data (e.g. discharge, sediment concentration, mercury in water and sediment, etc.).

An effective solution, which could be implemented relatively rapidly, would be to flag in the sediment and water quality data publications the stations which have sediment or water quality data published under another cover. This would alert the data user to the existence of additional data, while leaving the publications in their present, recognized forms.

IT IS RECOMMENDED THAT METHODS OF PUBLISHING DATA, WHICH HIGHLIGHT TO THE USER THE EXISTENCE OF OTHER PHYSICAL AND CHEMICAL SEDIMENT DATA, BE EXAMINED.

6) Data Interpretation

WQB and WRB personnel should jointly write interpretive reports, with input as required from the research institutes. To do this effectively physical, chemical and biological information must be integrated and synthesized. In this way the expertise and information that IWD has responds to the primary objective of assessing the effects of contamination on the ecosystem. Specific expertise is required for the sound treatment of each subject; one cannot readily adopt the other and create a high quality, scientifically sound product.

Environmental quality interpretive reports should be initiated by WQB. Assistance from WRB and researchers would be required for presenting sediment regime information and working closely with and providing advice to WQB staff regarding interpretation of sediment chemistry data. Upgrading of WRB staff would be required to carry out this function.

IT IS RECOMMENDED THAT WQB AND WRB COLLABORATE WHERE APPROPRIATE IN THE INTERPRETATION OF THE PHYSICAL AND CHEMICAL SEDIMENT DATA USED IN WATER QUALITY ASSESSMENTS.

7) Implementation of Recommendations

There is a growing understanding that water quality factors depend strongly on hydrological and geomorphological events. For this reason it can be expected that individuals in each Branch will

increasingly approach individuals in the other Branch or Research Institutes for expertise or advice in areas of mutual concern. Managers in each Branch are also encouraged to involve the other in the planning of projects on which interaction would lead to more complete environmental information.

Developing the knowledge base of staff in WQB and WRB with respect to all aspects of sediment chemistry should be a high priority. This could be done through workshops, seminars, etc. Experience of staff in research institutes, consultants and academics should be drawn upon as much as possible.

5. FUTURE CONSIDERATIONS

Sediment-water quality relationships are a developing science. While many aspects are known and can be incorporated in WQB & WRB programs, a host of others remain poorly understood. For this reason strong guidance and input from the research sector is required at all stages of program establishment and evaluation. Several areas of research are identified here due to their immediate importance to water quality assessments; physical sediment dynamics, sediment-water interactions and environmental effects of sediment-contaminant complexes.

An understanding of physical sediment sources, transport dynamics and fate is needed to carry out complete impact assessments. Tracing sources of "mystery" compounds necessitates a knowledge of the basin sediment regime and of the sediment sources. This would define a maximum possible zone of sediment-contaminant origin. Data for trends and objectives development do not require sediment source information as the "source" is considered to be the site of liaison of the sediment and contaminant.

Knowledge of sediment-water interactions is essential for correct interpretation of data on long term trends, for impact assessments and for development of objectives. Under what sets of conditions (seasons) will contaminants become/stay associated with sediments? for how long? what conditions trigger contaminant release?

The interaction processes (sediment-water equilibrium dynamics) govern the relative contaminant levels in media and the potential effects. Observation of a long term trend in sediment-contaminant levels may, for example, reflect a change in acidity rather than a change in contaminant amounts. Estimated effects could be grossly inaccurate if the relevant processes are not understood.

Intimately tied in with phase interactions is the issue of bioavailability and bioeffects. Available species in each phase, concentration and duration of exposure under diverse conditions, bio-uptake under varying conditions and physiological effects on bioavailability have been well studied in the laboratory, but have uet to be researched under field conditions. Without field testing, contaminant impacts and effects on the aquatic biota remain largely conjecture. Developing appropriate objectives for the protection of aquatic life would thus not be possible. Recent sediment-bioassay work, which indicates potential toxicity of sediment-contaminant complexes, is promising as a means of evaluating biological effects and for the development of water quality objectives.

Specific areas of research required to refine operational procedures of sediment activities include the study of sampling strategies for suspended sediment, accuracy and compatability of field and analytical procedures, existing data records (with respect to amount of extractable information) and sediment banking (storage for retroactive analysis).

6. REFERENCES

(References listed are those found in the text as well as the appendices.)

Allan, R.J. 1986. The Role of Particulate Matter in the Fate of Contaminants in Aquatic Ecosystems. Scientific Series No. 142. Inland Waters Directorate, National Water Research Institute, Canada Centre for Inland Waters.

Allan, R.J., T. Brydges, D. Dodge, R.D. Hamilton, D.G. Jeffs, K. Shikaze. 1984. Mercury Pollution in the Wabigoon-English River System of Northwestern Ontario and Possible Remedial Measures. Final Report of the Steering Committee, Volume 1 and 2, 570 pp.

Ashmore, P.E. 1986. Suspended Sediment Transport in the Saskatchewan River Basin. Internal Report, Inland Waters Directorate. IWD-HQ-WRB-SS-86-9.

Blachford, D.P., E.D. Ongley, 1984. Biogeochemical pathways of phosphorus, heavy metals and organochlorine residues in the Bow and Oldman rivers, Alberta, 1980-1981. Sci. Series No. 138, Water Quality Branch, Inland Waters Directorate, Ottawa.

Bopp, R.F., H.J. Simpson, C.R. Olsen, N. Kostyk, 1981. PCBs in sediments of the tidal Hudson River, New York. Envir. Sci. Technol. 15: 210-216.

Brannon, J.M., J.R. Rose, R.M. Engler, I. Smith, 1976. The distribution of heavy metals in sediment fractions from Mobile Bay, Alabama. In: Chemistry of Marine Sediments. Yen, T.F., Ed. Ann Arbour Sci. Publ. pp 125-149.

Bynoe, M.C. 1979. Spatial and Temporal Trends in the Fluvial Transport of Sediment-Related Heavy Metals in Wilton Creek, S.E. Ontario. M.Sc.Thesis, Queen's University, Ontario.

Canadian Council of Resource and Environment Ministers. 1985. Inventory of Water Quality Guidelines and Objectives 1984. Prepared by CCREM Task Force on Water Quality Guidelines.

Chapman, P.M., G.P. Romberg, G.A. Vigers. 1982. Design of monitoring studies for priority pollutants. J. Wat. Poll. Contr. Fed. 54(3):292-297.

Conservation Management Systems. 1985. Ontario Perspectives on Sediment Issues - Phase 1. Interim Report. Consulting Report. IWD-HQ-WRB-SS-85-4.

Day, T.J. and M.O. Spitzer, 1985. Sediment Station Analysis, Oldman River New Brocket. 05AA024. Internal Report to Inland Waters Directorate.

Dickinson, W.T. and Wall, G.T. 1977. Temporal and Spatial Patterns in Erosion and Fluvial Processes. In: Research in Fluvial Systems. R. Davidson-Amott and W. Nickling (eds.) Geo Books, Norwich p.p. 138-148.

Edgington, D.H., E. Callender. 1970. Minor element geochemistry of Lake Michigan ferromanganese nodules. Earth Planet. Sci. Lett. 8:97-100.

Federal Inter-Agency River Basin Committee, 1953. Accuracy of sediment size analyses made by the bottom withdrawal tube method. Report No. 10. Project Offices of Cooperating Agencies, Minnesota.

Fisher, J.B., W.J. Lick, P.L. McCall. 1980. Vertical mixing of lake sediments by tubificid oligochaetes. J. Geophys. Res. 85(7): 3997-4000.

Forstner, U. 1977a. Metal concentrations in freshwater sediments - natural background and cultural effects. In: Interactions Between Sediments and Freshwaters, Golterman, H.L., Ed. p. 94-103. Junk/Pudoc, The Hague.

Forstner, U., S.R. Patchineelam, 1976. Bindung und mobilisation von schwermetallen in fluviatilen sedimenten. Chem. Z. 100:49-57. In: Metal Pollution in the Aquatic Environment. Forstner, U., G.T.W. Whittmann, 1981. Springer-Verlag.

Forstner, U., G.T. W. Whittmann, 1981. Metal Pollution in the Aquatic Environment. Springer-Verlag. 486 pp.

Frank, R., R.L. Thomas, H.E. Brau, D.L. Gross, T.T. Davies. 1981. Organochlorine insecticides and PCB in surficial sediments of Lake Michigan. J. Great Lakes Res. 7:42-50.

Gibbs, R.J. 1977. Transport phases of transition metals in the Amazon and Yukon Rivers. Geol. Soc. of Am. Bull. 88:829-843.

Gupta, S.K., K.Y. Chen. 1975. Partitioning of trace metals in selective chemical fractions of nearshore sediments. Envir. Letters 10:129-158.

Hall, D.G. 1967. The pattern of sediment movement in the River Tyne. In: River Morphology. Proc. Bern Symp. 1967, I.A.H.S. Publ. No. 75:117-140.

Heidel, S.G. 1956. The progressive lag of sediment concentration with flood waves. Am. Geophy. Union Trans. 37(1):56-66.

Hugget, R.J., M.E. Bender. 1980. Kepone in the James River. Environ. Sci. Technol. 14:918-923.

Hydrotech Inc. 1985. Etat de Connaissance et Prospectives Sedimentologiques des Eaux Douces du Quebec. Rapport Consultatif. IWD-HQ-WRB-SS-85-7.

James, R.O., T.W. Healy. 1972. Adsorption of hydrolyzable metal ions at the oxide-water interface. J. Colloid Interface Sci. 40:42-52, 65-81.

Jenne, E.A. 1976. Trace element sorption by sediments and soils - sites and processes. In: Symposium on Molybdenum. Chappell, W., K. Petersen, Eds. Vol. 2. Marcel Dekker, N.Y. pp. 425-553.

Jennett, J.C., B.G. Wixson. 1975. The new lead belt: aquatic metal pathways-control. In: International Conference on Heavy Metals in the Environment. Sym. Proc. Vol. 2:247-255.

Jinks, S.M., M.E. Wrenn. 1976. Radiocesium transport in the Hudson River estuary. In: Environmental Toxicity of Aquatic Radionuclides: Models and Mechanisms. H.W. Miller, J.N. Stonnards, Ed. Ann Arbour, Ann Arbour Sci., p. 207-227.

Jonasson, I. 1977. Geochemistry of sediment-water interactions of metals, including observations on availability. In: The Fluvial Transport of Sediment-Associated Nutrients and Contaminants. H. Shear, A. Watson. I.J.C. pp. 255-271.

Kellerhals Engineering Services Ltd. 1985. Sediment in the Pacific and Yukon Region: Review and Assessment. Consulting Report. IWD-HQ-WRB-SS-85-8.

Kellerhals, R., A.D. Abrahams, H. von Gaza, 1974. Possibilities for using Suspended Sediment Rating Curves in the Canadian Sediment Survey Program. Univ. of Alberta, Dept. of Civil Engineering. Consulting Report.

Kuntz, K.W. 1982. Loadings to Lake Ontario by the Niagara River. Water Quality Branch, Inland Waters Directorate, Ontario Region, Environment Canada.

Kuntz, K.W., N.D. Wary. 1983. Chlorinated organic contaminants in water and suspended sediments of the lower Niagara River. J. Great Lakes Res. 9(2): 241-248.

Linsalata, P., H.J. Simpson, C.R. Olsen, N. Cohen, R.M. Trier. 1985. Plutonium and radiocesium in the water column of the Hudson River estuary. Envir. Geol. Water Sci. Vol. 7(4):193-204.

Nissenbaum, A. 1972. Distribution of several metals in chemical fractions of sediment core from the Sea of Okhotsk. Isr. J. Earth Sci. 21:143-154.

Northwest Hydraulic Consultants Ltd. 1985. Assessment of Sediment Issues and Survey Program in the Prairie Provinces. Consulting Report. IWD-HQ-WRB-SS-85-5.

Northwest Hydraulic Consultants Ltd. 1986. Sediment Station Analysis: Saskatchewan River at The Pas, 05KJ001. Consulting Report to Inland Waters Directorate. IWD-WNR(W)-WRB-SS-86-1.

Ong, H.L., R.E. Bisque. 1968. Coagulation of humic colloids by metal ions. Soil Sci. 106(3):220-224.

Ongley, E.D., M.C. Bynoe, J.B. Percival. 1981. Physical and geochemical characteristics of suspended solids, Wilton Creek, Ontario. Can. J. Earth Sci. 18(8):1365-1379.

Pearce, P.H., F. Bertrand, J.W. MacLaren. 1985. Inquiry on Federal Water Policy. Final Report. Environment Canada.

Pionke, H.B., G. Chesters. 1973. Pesticide-sediment-water interactions. J. Envir. Quality. 2:29-45.

Reuter, J.H., E.M. Perdue. 1977. Importance of heavy metal-organic matter interactions in natural waters. Geochim. Cosmochim. Acta. 41:325-334.

Robinson, M.W. 1972. Sediment Transport in Canadian Streams: A study in Measurements of Erosion Rates, Magnitude and Frequency of Flow, Sediment Yields and some Environmental Factors. M.A. Thesis, Carleton University.

Salomons, W., U. Forstner. 1980. Metals in the Hydrologic Cycle. Springer-Verlag, 350 pp.

Saxby, J.D. 1973. Diagenesis of metal-organic complexes in sediments: formation of metal sulphides from cysteine complexes. Chem. Geol. 12:241-288.

Shuman, M.S., C.L. Haynie, L.A. Smock. 1978. Modes of metal transport above and below waste discharge on the Haw River, North Carolina. Envir. Sci. Technol. 12(9):1066-1069.

Singer, P.C. 1977. Influence of Dissolved Organics on the Distribution transport and fate of heavy metals in aquatic systems. In Fate of Pollutants in the Air and Water Environments. Part I. Suffit, IH (Ed) John Wiley and Sons, p. 155-182.

Tessier, A., P.G.C. Campbell, M. Bisson. 1980. Trace metal speciation in the Yamaska and St. Francois Rivers (Quebec). Can. J. Earth Sci. 17:90-105.

Thomas, R.L. 1983. Lake Ontario sediments as indicators of the Niagara River as a primary source of contaminants. J. Great Lakes Res. 9(2):118-124.

Thomas, R.L., J.-M. Jaquet. 1976. Mercury in the surficial sediments of Lake Erie. J. Fish. Res. Board of Canada 33:404-412.

Thomas, R.L., A. Mudroch. 1979. Small Craft Harbours-Sediment Survey: Lake Ontario, Erie and St. Clair. Report to Small Craft Harbours Ontario Region. December 1979, 149 pp.

Turk, J.T. 1980. Applications of Hudson River basin PCB-transport studies. In: Contaminants and Sediments. R.A. Baker, Ed., Ann Arbour Science Pub., Ann Arbour, Michigan, p. 171-184.

Tywoniuk, N., M.A. Cashman. 1973. Sediment distributions in river cross-sections. Proceedings of the Ninth Canadian Hydrology Symposium on Fluvial Processes and Sedimentation, Univ. of Alberta.

Vuceta, J., J.J. Morgan. 1978. Chemical modeling of trace metals in freshwaters: role of complexation and adsorption. Envir. Sci. Technol. 12(2):1302-1309.

Walling, D.E. 1977. Assessing the accuracy of suspended sediment rating curves for a small basin. Wat. Resour. Res. 13:531-538.

Washburn & Gillis Associates Ltd., 1985. Freshwater Sediment Data Collection and Use in the Atlantic Provinces. Consulting Report. IWD-HQ-WRB-SS-85-6.

Water Quality Branch, 1979. Analytical Methods Manual. Inland Waters Directorate, Ottawa.

Water Quality Branch, 1986. Water Quality Branch Strategy for Assessments of the Quality of Aquatic Environments. Inland Waters Directorate, WQB, Ottawa. IWD Sci. Series No. 151. 17 p.

Water Quality Branch, 1986. The Need for an Assessment Strategy on the Exposure and Effects of Contaminants in the Aquatic Environment. Inland Waters Directorate, Ottawa. Draft.

Water Resources Branch, 1984. Laboratory Procedures for Sediment Analysis. First Edition. Sediment Surveys Section, Inland Waters Directorate, Ottawa.

Watt, E., A. Demayo, M. Forbes. 1984. Polynuclear aromatic hydrocarbons in bottom sediment samples of rivers, lakes and harbours. Water Quality Branch, Environment Canada, Ottawa. Unpubl. Report.

Wedepohl, K.H. 1972. Zinc abundance in natural waters and in the atmosphere. In: Handbook of Geochemistry. Wedepohl, K.H., Ed. Springer.

Wedepohl, K.H. 1974a. Copper abundance in natural waters and in the atmosphere. In: Handbook of Geochemistry. Wedepohl, K.H., Ed. Springer.

Whitfield P.H., H. Schreier. 1981. Hysteresis in relationships between discharge and water chemistry in the Fraser River basin, British Columbia. Limnol. Oceanogr. 26(6):1179-1182.

APPENDIX I.

SEDIMENTS AND WATER QUALITY: BACKGROUND SCIENTIFIC INFORMATION

Sediment quality issues and the use of sediments in water quality assessments were briefly reviewed in Chapter 2. Chapter 3 presented data and sampling design requirements. This Appendix provides further information on the former and substantiates the latter. Information is presented according to the roles of sediment, as stated earlier:

1) identifiers of contaminant presence;
2) contaminant transport and fate; and
3) regulators of contaminant partitioning between aqueous and biological compartments.

I.1 IDENTIFIERS OF CONTAMINANT PRESENCE

The roles that sediments play in the evaluation of water quality are substantially due to the ability of sediment to accumulate substances such as organic contaminants, metals and nutrients. Sediments concentrate contaminants to levels which may be readily detectable by conventional methodology. Because of the greater amount associated with the sediment, and the fact that the concentration of sediment-associated contaminant represents an amount integrated over a period of time (rather

than an instantaneous amount represented by a water sample), sediment samples are mandatory for documenting baseline levels in the aquatic system and for establishing long term trends.

A multitude of factors affect the ability of sediments to scavenge substances from the water column. Particle size influences the sorption capacity of sediments as well as determining the mode and distance of transport and sedimentation rate. The organic content of a sediment sample has been found to greatly influence the particulate-associated amount. Knowledge of the mechanisms by which the substances associate with particulate matter is essential for estimating biological availability and physicochemical activity. Concentrations and characteristics of the contaminants also influence the extent and duration of association with the particulate phase. Particle size and organic content of the sediments and sediment-contaminant bonding mechanisms are discussed below.

Particle Size

The particle size distribution of fluvial sediments are determined by physical processes of erosion, transport and deposition. A large portion of the fluvial transport of sediment in Canada occurs in the form of suspended material with particle sizes in the silt range (2-62µm: note that WQB defines the lower silt range at 2µm while WRB has 4 µm which is the accepted value needed in physical sedimentation

work). During low flow periods, minimal amounts of material are mobilized and carried, and suspended matter may be deposited and incorporated into the bottom sediment. Higher flows mobilize the bed and river bank materials. The clay-size (<2μm) fraction tends to remain in suspension and settles out only after prolonged periods of time. The fine fraction (≤62μm, silt and clay) of the sediment load varies in amount, range of sizes, sediment source and with the hydrologic regime. This size fraction is largely responsible for accumulating and carrying substances over long distances.

Solid particles with small diameters have large surface areas and the highest adsorption potential. An increase in surface area results in increased adsorption of a suite of substances. Gibbs (1977) noted that small particles have the highest concentrations of all the transition elements.

The dependency of metal concentration upon size fraction has been observed by many researchers. Given the same volume of sediment, there is more surface area in a sample with smaller particle sizes. Different proportions of substances present in solution are adsorbed, with orders of magnitude difference, at varying amounts of available surface area (Vuceta and Morgan, 1978). For example, concentrations of zinc and nickel in sediments from Lake Constance and the Lower Rhine show a distinct increase from coarse to fine-grained fractions (Forstner and Whittmann, 1981). Slight concentration decreases in the <2μm and

increases in the >62μm fractions result, respectively, from reduced adsorption potential of partially less crystalline or amorphous substances and from the occurrence of detrital minerals rich in metals. The greatest anthropogenic enrichment occurs in the clay and silt fractions. Gibbs (1977) found that a greater amount of metal (90% of the iron, for example) in the Amazon River is transported in an intermediate (0.2μm to 20μm) size range due to the larger number of particles in this size fraction.

Concentrations of metals in different bonding associations with particles vary in distribution with size. The concentration of iron in the hydrous oxide state, for example, is in the 1-2μm range whereas the maxima in the residual (crystalline) phase is approximately 10μm (Gibbs, 1977).

The importance of grain size distribution information was emphasized in a study by Watt et al. (1984). Polynuclear aromatic hydrocarbons, readily sorbed onto suspended matter, were analyzed in bottom sediments in the vicinity of various land uses and processing plants. However, site differences in concentration could not be meaningfully compared due to lack of particle size information.

On the other hand, a study of toxic contaminants in the Niagara River (Kuntz, 1982) found that metals and organic contaminant concentrations did not appear to be significantly related to adsorptive

capacity such as percentage of silt and clay. Concentrations were influenced by location of input sources and/or current velocity in the sampled area.

It is clear from the above that contaminant analysis of bulk sediment samples, whether for background data or for pollution control purposes, requires grain size information. Without a correction for grain size, particularly in fluvial environments where seasonal granulometric changes may be pronounced, sediment analyses collected for monitoring programs would be of little significance.

Organic Content

Suspended and bottom sediments are composed of inorganic and organic materials, derived from sources outside or within the water body. The inorganic material consists of erosion products from rocks in the watershed and compounds formed from soluble products in the water column. The organic material consists of plant and animal products in various stages of decomposition, of compounds synthesized biologically and chemically from the breakdown products and of microorganisms and their decomposing remains. The mineral and organic proportions of the total sediment load vary seasonally and in geochemical importance.

Aquatic biota is receiving increasing recognition for its role in solid-aqueous partitioning. The biota is capable of accumulating

contaminants many orders of magnitude over concentrations present in ambient waters, and in quantities above those required for growth. Jennett and Wixson (1975) found that algae and macrophyte communities were 99% effective in removing heavy metals from waters draining the lead-zinc mining region of the Ozarks. Pionke and Chesters (1973) found that aquatic vegetation could accumulate certain pesticides to concentrations 100-10 000 times those found in water. Aquatic plants may alter the phase distribution of contaminants not only by direct assimilation but also by trapping contaminant-rich mineral particulates and by serving as a substrate for epiphytes and mineral encrustation with their associated binding capacities. Fauna, such as benthos and fish, are also capable of assimilating large quantities of contaminants thereby altering concentrations in the aqueous phase.

The significance of biota is not limited to their role as temporary reservoirs of contaminants. Aquatic vegetation may release accumulated substances by secretion over the growing season and during decomposition. The latter process also contributes seasonal slugs of contaminant-rich organic fragments which became incorporated into the particulate load. Decomposition produces highly reactive colloidal fragments, which are in themselves effective scavengers in the aquatic milieu. Substances accumulated by aquatic fauna may be returned to the system via decomposition; the environmental significance of the assimilated substances, however, lies in their potential biomagnification in the food web.

The dominant products of decomposition of organic matter (aquatic and terrestrial biota) are the humic substances. These comprise 60-80% of the dissolved and particulate organic carbon in fresh waters (Reuter and Perdue, 1977). Contaminants have a high affinity for organic substances as they may chemically attach to the aromatic core of the humic substances. In dissolved or particulate form, stable complexes can form between the organics and charged ions such as calcium, iron and mercury. Dissolved organic matter influences the distribution, transport and fate of contaminants by:

1) complexing metals and increasing their solubility (potentially increasing toxicity);
2) altering the distribution between oxidized and reduced forms;
3) alleviating toxicity and altering availability of attached substances;
4) influencing the extent to which metals are adsorbed to suspended matter; and
5) affecting the stability of colloid-contaminant complexes (Singer, 1977).

The importance of the particulate organic portion of the total sediment load has been recognized for many years. The Amazon and Yukon Rivers carry as much as one-third of the total chromium and cobalt and one-quarter of the total nickel load in association with particulate

organics (Gibbs, 1977). Shuman et al. (1978) found that the proportion of total metals bound to organic particulates increased at polluted sites. A study of bottom sediments from Lake Malawi indicated that zinc, copper and vanadium were accumulated in association with organic materials whereas iron, manganese, chromium, cobalt, lead and nickel were diluted by the organic matter. Similarly, Blachford and Ongley (1984) noted elevated levels of some metals during times of higher organic loading and dilution of iron and nickel in suspended sediments of two rivers in western Canada. Thomas and Jaquet (1976) found a stronger correlation of organic content with natural mercury levels than with anthropogenically influenced levels.

It must be recognized that a positive correlation between organic content and contaminant concentration is not necessarily a result of contaminant scavenging by organic substances. Other mechanisms, such as adsorption by clays and oxides, produce simultaneous accumulation of organics and contaminants. In highly polluted areas, accumulation of metals coincides with that of organic substances, both derived from urban, industrial and agricultural sewage effluents.

Bonding Mechanisms

Mineral and organic sediment complexes act as sinks and transporters of substances by means of physical and chemical bonding mechanisms. Knowledge of the associations provides an indication of the biological exposure and potential effects. As the mechanisms are

environmentally mediated, sediments may release the bound substances under varying physicochemical conditions. Association of contaminants with solid substances can be characterized by the following bonding processes:

1) adsorption;
2) coprecipitation with hydrous iron and managanese oxides;
3) complexation by organic molecules; and
4) incorporation in the crystalline matrix.

Table 1 indicates carrier substances and their associated mechanisms of bonding.

Adsorption (1) is the process whereby minerals with large surface areas may accumulate ions as a result of intermolecular forces. The charge of a clay mineral particle is usually negative and it therefore attracts cations. The balancing of the negative charge of the particle is a competitive process which accounts for the preferential adsorption of some cations and the release of others with equivalent charges. The affinity of ions for charged surfaces is determined by factors including valence, hydration (Ong and Bisque, 1968), state of hydrolysis (James and Healy, 1972), concentration of solution, pH and specific reactions.

Observations in fluvial systems have shown that the fraction of sediment-associated metals transported in the adsorbed form (rather than in the hydrous oxide, crystalline or organic complex forms) is relatively

Table 1

CARRIER SUBSTANCES AND MECHANISMS OF

HEAVY METAL BONDING

Minerals of natural rock debris e.g. heavy minerals		Metal bonding predominantly in inert positions
Heavy metal - hydroxides - carbonates - sulfides		Precipitation as a result of exceeding the solubility product in the area of the water course
Hydroxides and oxides of Fe/Mn	pH-dependent	Physico-sorption Chemical sorption (exchange of H^+ in fixed positions) Coprecipitation as a result of exceeding the solubility product
Bitumen, lipids Humic substances Residual organics	pH-dependent	Physico-sorption Chemical sorption (exchange of H^+ in COOH-, OH-groups) Complexes
Calcium Carbonate	pH-dependent	Physico-sorption Pseudomorphosis (dependent on supply and time) Coprecipitation (incorporation by exceeding the solubility product)

Source: Forstner and Patchineelam, 1976.

insignificant (Tessier et al., 1980, Gibbs, 1977). This may be due to other processes which reduce the metal content in solution before adsorption can occur (Forstner and Whittmann, 1981). The minor proportion of total sediment-related metal associated with the adsorbed phase, however, may be important in view of the absolute amount of solid-related metal that may be released and thereby become bioavailable. The significance of fine particles in the sorption of metals may lie in their role as a substrate for the precipitation and flocculation of organics and hydrous iron and manganese oxides.

Hydrous oxides of aluminum, iron and manganese (2) constitute significant sinks of metals in aquatic systems (Forstner and Whittmann, 1981). Hydroxides modify metal phase distributions by readily sorbing or coprecipitating cations and ions. The process occurs by a combination of surface exchange and specific adsorption. Precipitates form on solids when the solubility product of a compound is exceeded. Various substances may coprecipitate with the hydroxides. Accumulation of substances on and/or with the hydroxides is governed by conditions such as pH, concentration of the solution, number of competing ions and the presence of dissolved and particulate organic complexes.

Metallic hydroxide coatings are the solid phase most likely to control the concentration of solutes in the Yukon and Amazon Rivers (Gibbs, 1977). Tessier et al. (1980) found metal concentrations associated with iron and manganese oxides constituted a large proportion

of the nonresidual metals in two Quebec rivers. Hydrous oxides played important roles as metal scavengers in Canadian subarctic lakes with low organic content (Jonasson, 1977). The role of hydroxides as scavengers in organic systems is overshadowed by competition from more reactive organic compounds (Jonasson, 1977).

Soluble, colloidal or particulate organic material (3) may bind with ions by physical adsorption (in which case the ions are easily replaceable) or by strong, chemical-like bonds. Jenne (1976), suggested that the portion of metals in natural waters as a soluble organic complex is greater than that present in inorganic form. Metal-organic complexes may associate with sediments by the following processes (Saxby, 1973):

a) direct precipitation or adsorption of metal-organic species. The association with clay minerals is particularly important. Metals interact with dissolved organic carbon, which is then concentrated by adsorption onto particulates;
b) incorporation of metal-rich, decaying organisms;
c) sediment adsorption of molecules resulting from dissolution of minerals by waters with organic ligands.

Metals can be transported as major, minor or trace components in natural rock debris (4). The metals are frequently locked in inert lattice positions. The distribution of elements in minerals is determined by the source of formation and by crystal-chemical factors

(e.g. ionic radius, valences) (Wedepohl, 1972, 1974a). Feldspar and quartz usually have very low metal contents. Copper is not readily incorporated whereas zinc and lead are preferentially incorporated into distinct structural positions of silicates and oxides.

I.2 CONTAMINANT TRANSPORT AND FATE

There is a dynamic equilibria between contaminants in water and in sediments and biota. Phase changes can be expected to occur while in transport and over time. Physical and chemical conditions of the water and properties of the contaminant itself, determine the media with which the contaminant becomes associated. As many of the contaminants of present day concern are hydrophobic, suspended and bottom sediments are primary sinks in aquatic systems. Once in association with the sediments, the spatial and temporal distribution of the contaminants is governed by the hydrologic and sediment regimes. Location of transport, media, in-stream storage, area of deposition and burial, potential for recycling and bioavailability are determined by fluvial dynamics and the contaminant- solid relationship. The nature of the contaminant-sediment relationship may indicate the source (natural or anthropogenic) and bioavailability of the contaminant.

Sediment-contaminant transport processes are discussed here under the headings:

1) Sediment Dynamics;

2) Fractionation of Sediment-Related Contaminants; and

3) Seasonality.

Use of sediments as tracers of contamination responds to the water quality assessment goal of information provision for environmental impact assessment.

Sediment Dynamics

Knowledge of water and sediment regimes is essential for understanding the spatial and temporal distribution and variability of the presence and potential effects of the sediment - contaminant complex. It is also required for designing a basin specific sampling program based on determining the presence, effects and fates of sediment-associated contaminants within the system.

In considering sediment dynamics a number of aspects must be taken into account. These include: nature and properties of sediments; definitions (bed material, bed load, suspended, wash load, etc.); transport mechanisms; sources; transport pathways and fate (deposition). Most of these aspects are adequately covered in either textbooks or articles (e.g. Golterman et al. 1983, Allan, 1986). For this discussion the key aspects, in order of emphasis, are: transport of suspended sediments, their fate and source.

Once contaminants are adsorbed onto suspended sediments their measurement and tracing within fluvial systems is essentially a physical sediment concern. This means that even though field sampling and analytic methods for sediment associated contaminant may vary from traditional physical sediment procedures, the interpretation of concentration and calculation of loadings relies upon an understanding of suspended sediment transport - in particular the fine sizes.

In considering suspended sediment transport the important aspects are regime and cross-sectional variations. By regime is meant the time-distribution of concentration, particle size and loading. As with hydrologic regime, suspended sediment regimes are marked by annual and seasonal variations. Also, at any point along a river system regime characteristics vary over time according to the imposed hydrologic regime, upstream sediment sources and the upstream channel system (i.e. presence of lakes, overbank storage, etc.).

Suspended sediment regime is key to the interpretation of measurements of sediment-associated contaminants as the sediment acts as a dilutant of the contaminant in the same way water dilutes dissolved substances. It is the sediment which becomes the transporting medium.

Our knowledge of suspended sediment regimes in Canadian river systems is quite sound. Sediment monitoring activities of Water Survey of Canada began in the early 1960's and data (in varying amounts) now

exist for over 700 sites across the country. More recently attention has focussed upon interpreting these data in fact to document regime characteristics and assess the adequacy of the data base.

These interpretive studies (e.g. Day and Spitzer, 1985; Northwest Hydraulic Consultants, 1986; Ashmore, 1986) demonstrate that suspended sediment regimes, while varying greatly due to geographic setting, flow regime, etc., are commonly much more variable (on annual and seasonal time frames) then hydrologic regimes. They can be dominated by infrequent large events which carry major amounts of both annual and historic loads. These lakes and reservoirs in particular control the fate and pathways of sediments through the river systems.

Variations on short time scales again are much greater than for flow. Individual sediment events may or may not coincide with flow events. Supply depletion also 'distorts' the difference between flow and suspended sediment regime. This factor can result in hysterisis relationships between suspended sediment concentrations and water discharge. In some situations clear relationships between these two parameters do not exist. These and other factors clearly complicate the sampling and the interpretation of sediment-associated contaminants.

Sampling for sediment-associated contaminants can be further complicated by vertical and lateral variations of particle size and concentration in the river section. These variations, caused by channel

dimensions, hydraulics and available particle sizes, can be large for the fine, wash load sediments. The occurrence and significance of these variations have not been satisfactorily assessed.

The characteristics of suspended sediment regime particularly where wash load is of importance, are simply so variable that an adequate discussion is impossible. It is better to review the station analysis reports prepared by the Water Resources Branch noted earlier in the section, or other sources such as Dickinson and Wall (1977) and Robinson (1972).

Similarily the consideration of sediment sources is beyond the capability of this report. However, it is important to consider source areas as they not only largely determine the sediment characteristics, but they represent the important sites for land/water interface, and also serve to dilute contaminants as sediment is supplied along a river course.

Finally, the fate of sediment along river systems is of fundamental importance. The recent work by Allan (1986) provides an excellent assessment. In considering monitoring designs for sediment associated contaminants, care must be taken to understand deposition/loss/exchange of sediments along the river system. As noted by Northwest Hydraulics Consultants Ltd. (1986) and Ashmore (1986) the various reservoir developments along the Saskatchewan River system serve as sinks for suspended sediments. The location of such sinks is

an essential factor to be considered in tracing and monitoring sediment transport.

Suspended sediments are also lost or temporarilly stored along channels on floodplains and in back water areas. If toxic, these sediments can pose a direct problem. This exchange of sediments with boundary materials can also lead to either loss or gain of contaminated sediment.

Fractionation of Sediment-Related Contaminants

The bonding mechanisms of substances with sediments were discussed in section 2.2; the mechanisms are the actual physical and chemical means of association. In order to study these mechanisms, sets of procedures have been developed for estimating the various chemical forms. It must be emphasized that the fractionation procedures partition metals into fractions defined by the method of extraction, and do not necessarily reflect the relative amounts associated with the particulates by physical and chemical means. Chemical fractionation schemes are useful for estimating the speciation of particulate trace metals and nutrients in terms of their relative importance in controlling element transport and potential bioavailability. Metal and nutrient speciation studies have successfully identified pollution sources and spatial trends in geochemical behaviour and have highlighted areas of present or emerging concern.

Standardized methods for the fractionation of metals have not been established. Various methods evolved as interest in bonding forms in contaminated sediments developed (Table 2). The important information to be derived from the schemes is the proportion or amount of substance which may adversely affect the aquatic environment, i.e. the immediate or potentially bioavailable fraction of the total metal content.

Estimated fractions include:

1) adsorbed or exchangeable,
2) hydroxide
3) solid organic matter, and
4) detrital.

The easily exchangeable fraction (1) of solid-associated metal is considered to be the most bioavailable fraction in aerobic environments. It consists of elements loosely sorbed to mineral and organic sediments. Metals associated with the hydroxide fraction (2) are considered nonavailable in aerobic environments. Under anerobic conditions, however, reduction of the oxides may cause dissolution of attached elements.

Elements associated with organic matter (3) may be available following release during decomposition or by direct ingestion by aquatic organisms. After decay and mineralization of the organic matter, metals are considered nonavailable. Metals incorporated in detrital material (4) are inert and nonavailable.

Table 2

Extraction of Metals Associated with Different Chemical Phases in Sediments

CHEMICAL PHASE	EXTRACTION METHODS	AUTHORS
Adsorption and cation exchange	(a) $BaCl_2$ (b) $MgCl_2$ (b) NH_4OAc	Jackson, 1958: Gibbs, 1973
Detrital/autigenic phases	EDTA treatment	Goldberg and Arrhenius, 1958; Gad and Le Riche, 1966
Hydrogenous/lithogenous phases	(a) 0.1 M HCl(c)0.3 M HCl (b) 0.1 M $HCNO_3$	Piper, 1971 Jones, 1973; Malo, 1977
Reducible phases	1 M NH_2OH . HCl;25% v/v acetic acid	Chester and Hughes, 1967
Moderately reducible phases (hydrous Fe-oxides)	Oxalate buffer Dithionite/citrate buffer	Schwertmann, 1964 Holmgren, 1967
Easily reducible phases (Mn-oxide and amorph. Fe-oxides)	0.1 M NH_2OH . HCl;0.01 M nitric acid	Chao, 1972
Carbonates	(a) CO_2 treatment (b) Exchange columns (c) NaOAc/HOAc buffer	Patchineelam, 1975 Deurer et al., 1978 Tessier et al., 1979
Organics sulphides	30% H_2O_2 at 95°C, extract with (a) 1 N NH_4OAc or (b) 0.01 M HNO_3, fat solvents: e.g. chloroform, ether, gasoline, benzene, carbon disulfide	Jackson, 1958; Engler et al., 1974; Gupta and Chen, 1975 Bergmann, 1963 Welte, 1969 Cooper and Harris, 1974
Humic and fulvic acids	0.5 N NaOH;0.1 N NaOH/H_2SO_4	Rashid, 1971; Volkov and Fomina, 1974
Solid organic material	Na hypochlorite, dithionite/citrate	Gibbs, 1973
Detrital silicates	Digestion with HF/$HClO_4$; Lithium metaborate (1000°C)	

Source: Forstner and Whittmann, 1981.

Several studies have indicated that increases in metal levels in sediments due to pollution are accompanied by a change in the proportion of metals associated with the various fractions. Metals of anthropogenic origin tend to be carried in relatively unstable, potentially available bonding forms, whereas metals of natural origin are more firmly bonded with the sediment. For example, Gupta and Chen (1975) and Brannon et al. (1976) observed that as total metal levels rise in harbour sediments, concentrations in the detrital fraction decrease. The introduced anthropogenic metals were carried in non-detrital fractions. Similarly, Forstner (1977a), in studies of Rhine River sediments, distinguished a group of metals (iron, nickel, cobalt, chromium and copper) found in high proportions in the detrital, unavailable fraction and another group (lead, zinc and cadmium) found in non-detrital fractions. The latter group includes metals most related to anthropogenic activities.

The total amount and proportion of metals carried in suspended sediment fractions may be altered while in downstream transport by natural variations (discharge, sediment mineralogy and concentration, water chemistry) and by anthropogenic inputs. For example, the distribution of metals in sediment phases was established in the upper reaches of two Quebec basins. Variations occurred proceeding downstream due to metal inputs. Sediment-metal concentrations increased, the residual proportion decreased and hydroxide and organic coatings (potentially available) were the major metal sinks in the system (Tessier et al., 1980). Similarly, studies by Shuman et al. (1978) showed proportional increases in the available fractions of metals downstream of domestic and industrial waste inputs.

The proportion of metals associated with each fraction varies between basins, likely reflecting geochemical and geologic differences. For example, the unpolluted Amazon and Yukon Rivers carry chronium and cobalt in residual form and iron, manganese and nickel with hydroxide coatings (Gibbs, 1977). In contrast, Nissenbaum (1972) found iron and nickel predominantly in the residual fraction and manganese, copper and zinc with hydroxides in a sediment core from the Sea of Okhotsk.

Seasonality

The seasonal variability of sediment particle size and organic content, the discharge and sediment regimes and contaminant presence influences sediment-contaminant concentrations and their potential effects in the aquatic environment. Various studies are presented to highlight the seasonal flux of contaminant transport; the examples illustrate the interaction of many of the factors previously discussed.

A comprehensive study on rivers in Western Canada showed seasonal variations in contaminant phase partitioning, concentrations and loadings, and the influence of sediment concentration, size and organic content (Blachford and Ongley, 1984). Water, suspended sediment and aquatic plant samples were collected in spring, early summer, summer and fall at a total of 13 sites in the Bow and Oldman rivers. Each system contained one major point source of contamination: Calgary on the Bow and Lethbridge on the Oldman River. Seasonal observations on the concentrations of metals in 1) water, 2) sediments, and 3) plants include:

1) Metal levels in filtered and total water samples were largely below detection limits. Many of the detected metal levels were found in the total (soluble and particulate) samples in spring, when suspended sediment concentrations were more than an order of magnitude greater than in other reasons and comprised a larger proportion of clay-size particles.

2) Metal concentrations on suspended sediments were at an annual minimum in spring and peaked in summer and fall. Summer and fall concentrations of metals were higher than those in spring and early summer, due to the lower concentration of suspended sediment and therefore, a greater impact of metals from the point sources per unit weight of sediment. The organic content of the sediments peaks in summer and fall. Downstream trends within each season reflect point source inputs, elevated metal levels at sites of higher organic content and finer particle size, and release of metals to the water phase and subsequent association with sediments at a reservoir site. As for the metals, greater amounts of sediment-associated organic contaminants were observed in summer and fall, when suspended sediment was significantly higher in organic content, than in spring.

3) Concentrations of most metals associated with aquatic plants (macrophytes and algae) collected in summer and fall were frequently lower than those on suspended sediments. Concentrations reflect the amount of metals assimilated by the plant as well as that associated with attached epiphytes and with entrapped mineral sediment. Downstream trends in plant-metal levels reflected sites of metal availability in solutions that were not revealed by the water sample data.

Metal loadings over the sampled period were dominated by the high sediment load in spring. For the majority of metals, the sediment-associated load comprised most of the total load in water. Larger loads were calculated for the Oldman River, reflecting higher suspended sediment concentrations. The larger discharge of the Bow River produced greater loads during low-flow periods when both rivers had comparable sediment concentrations. Loadings of metals in plant material were generally greater than loadings in the water column; they represent a component of the bioavailable fraction which would likely be in the water phase if there was no in-stream vegetation. The plant-related metal load is transported as part of the suspended load during relatively short periods of time during senescence and decomposition (late summer and fall).

Similar observations on seasonality have been made by other researchers. Bopp et al. (1981) noted that the major transport of PCB in the Hudson River was during spring run-off and storm events when

suspended sediment concentrations were high. Hugget and Bender (1980) attributed the highest concentrations of PCB, DDT and Kepone in James River during the summer months to increase biological productivity and therefore increased partitioning to suspended organic particulates.

I.3 REGULATORS OF CONTAMINANT PARTITIONING

Many of the toxic contaminants in aquatic systems become strongly partitioned to mineral and organic suspended particulates. The toxics may be directly available to biota for uptake from the suspended solids, or may be removed temporarily from biological access due to sedimentation and burial. The deposited sediment-contaminants can be reintroduced to the ecosystem by internal recycling mechanisms. Remobilization of the contaminants may result in increased availability to the aquatic ecosystem.

Sediment-water interactions resulting in bioavailability of contaminants are diverse. Availability from bottom sediments involves interaction with overlying waters by sediment resuspension, bioturbation and pore-water release. Interactions in the water column take place between contaminants in solution and those present as colloids and suspended mineral and organic particulates, and the water medium. Although sediment partitioning of toxics reduces their availability from the aqueous phase, a considerably higher level of exposure to fish may result from ingestion of sediment than from ingestion of water over a

period of time due to the low concentration of toxics in water. For example, for compounds such as PCBs and Mirex which are accumulated by fish, one meal of fish can equal 20-25 years of human exposure from drinking water (Allan, 1983).

An understanding of the toxic-sediment recycling mechanisms will aid in the development of sediment and water quality objectives and in the provision of information for environmental impact studies. A brief review of:

1) physical processes;
2) chemical conditions; and
3) biological processes

of recycling and releasing contaminants associated with particulates is presented.

Physical processes (1) of toxic recycling involves sediment settling, burial and resuspension. Accumulation of contaminants in bottom sediments is well documented. Forstner and Whittmann (1981) showed the historical accumulation of metals in lakes, rivers and reservoirs; locations of input and bioavailability of the metals could be identified from the analysis of sediment core samples. Bottom sediments were identified as the primary sink for many toxic metals in a variety of European rivers. Bottom sediments of the Wabigoon River system

(Allan et al. 1984) are heavily enriched with mercury released from a chloro-alkali plant; cores from settling basins in the system show the accumulation over the twelve year operating time of the plant. The spatial distribution of toxic metals in the Great Lakes (Thomas & Mudroch, 1979) shows the accumulation of geologic and anthropogenic metal inputs.

Sediment-associated contaminants removed from lacustrine and fluvial water columns by sedimentation and buried after years of accumulation may be reintroduced by resuspension processes. Relevant physical processes in lakes include erosion of lake banks, wind generation of waves and currents and related suspended sediment circulation, and dune formation and migration. Physical processes in rivers are dominated by the discharge regime. For example, studies in the Hudson River of bottom sediments that continuously release PCBs in the overlying water found that in the lower range of discharges, PCB concentrations in total water samples rise as discharge falls. In the higher discharge range, however, concentrations rise as discharge increases. This is due to increased dilution and resuspension of bottom sediments (Turk, 1980).

A similar situation exists with mercury concentration and flow in the Wabigoon River (Allan et al, 1984). Methyl-mercury loads peak during high flow because of resuspension and transport of bottom sediments. Concentrations of methyl-mercury are low during high flow and

peak over the low-flow summer period. Regeneration of mercury from bottom sediments in the fluvial portions of the Wabigoon system is due to resuspension, while in the lake portions release of methyl-mercury to hypolimnetic waters is the observed recycling process. Positive relationships between surface sediment mercury concentrations and selected biota revealed the bioavailability of the solid-associated mercury. Decreased mercury concentrations in biota occurred following removal of the mercury source; sediment-mercury in the system was buried in the river and lake bottom sediments and was therefore less available for biological injestion. Slower declines in the biota since then reflect mercury regeneration from the bottom sediments, as well as deposition of contaminated sediment resuspended and transported from upstream locations. Both processes retard the cleansing of the system to background levels of mercury.

Chemical factors (2) regulating the release of sediment-related contaminants include:

a) salinity conditions;

b) redox conditions;

c) pH conditions; and

d) presence of organic complexing agents.

Salinity (a) increases in water lead to competition between the dissolved salts and substances adsorbed to solid particles, and may

result in replacement of the latter. Freshwaters may increase in salinity due to natural causes (e.g. mixing in an estuary; intensive bedrock-water interaction; area of low precipitation and high evaporation) or due to anthropogenic influences, (e.g. use of deicing salts; wastewater effluents; agricultural practices). Linsalata et al. (1985) noted the seasonal dependence of cesium solute/solid partitioning on chloride ion concentrations in the Hudson Estuary. During low freshwater discharge months, when saltwater intruded upstream, up to 90% of the cesium was found in the solute phase. Chlorinity was reduced during high freshwater discharge periods (spring runoff) and 50-80% of the water column cesium was observed in association with sediment particles. The proportion of cesium in solution has been shown to increase with chloride concentrations due to competition primarily from potassium for sediment sorption sites (Jinks and Wrenn, 1976). Total dissolved mercury increased with the dissolved chloride concentration in the Wabigoon River, possibly representing dissolution of mercury from sediments by the formation of water-soluble chloride complexes.

A change in the redox (reduction-oxidation) conditions (b) can cause release of sediment-attached substances to the water phase. A redox decrease may be caused by oxygen depletion resulting from incomplete mixing at the sediment-water interface in low velocity regimes, and from anthropogenic inputs and natural occurrences of organic material causing biological and chemical oxygen demands. Oxygen depletion triggers the conversion of, for example, insoluble ferric iron (Fe^{3+}) to the soluble ferrous (Fe^{2+}) form; any substances

coprecipitated with the iron are therefore remobilized. Edgington and Callender (1970) have calculated that increased eutrophication of Lake Michigan would significantly raise the arsenic concentration in the water due to dissolution of arsenic-containing ferro-manganese nodules.

An increase in acidity (c) leads to the dissolution of hydroxide and carbonate minerals and, as a result of hydrogen ion competition, to desorption of attached substances. Changes in pH along the course of a river may be caused by anthropogenic inputs (e.g. acid mine drainage, sewage treatment plants and industrial effluents, fallout from atmospherically transported pollutants) and by natural variations in, for example, bedrock geology and tributary inputs. Acid mine drainage may induce a 1 000-10 000-fold increase in metal concentrations.

Natural organic compounds (e.g. humic and fulvic acids) and synthetic complexing agents (e.g. polyphosphate replacements in detergents) may cause dissolution of metals from particulate material (d). Metals may be reduced by acids to more soluble states, or may form a soluble complex with the organic acids. Inputs of synthetic organics from sewage treatment plants and of natural acids from decomposing environments along a river may cause localized release of substances from suspended and bottom sediments.

Biological processes (3) of recycling sediment-related contaminants involve:

a) biologically-mediated transformations;

b) physical turbulence at the sediment-water interface (bioturbation);

c) bioaccumulation (incorporation of contaminants into organisms) and biomagnification (accumulation of contaminants in an organism by injestion of contaminant-containing organisms); and

d) scavenging from the water column and in the sediment bed by organic products of decomposition of aquatic organisms (discussed in Section 2.2).

Mobilization of contaminants associated with dissolved and particulate organic matter is largely mediated by microbial activity (a). The organic matter must be initially decomposed and the physical environment modified by metabolic activity prior to enzyme-catalyzed processes which convert inorganic compounds into organic substances capable of contaminant complexation. The bacterial conversion of sediment-mercury to soluble methyl mercury in the Wabigoon River is a well known example of this process. Biological methylation of arsenic, lead and selenium also occurs. The methylated forms of metals are available and highly toxic to aquatic organisms.

Benthic organisms play an important role in recycling sediment-contaminants into the food chain by the ability to rework surface sediments (b). Without mixing, sediments deposited over a period of time would eventually be buried and out of contact with surface

waters. Due to bioturbation, however, the contaminant concentration decreases towards the sediment surface with considerable amounts remaining in contact with overlying water and therefore potentially available for biological uptake. Turbificids, for example, mix sediments to depths of 6-9 cm by injesting sediment at depth and expelling it at the sediment-water interface (Fisher et al, 1980).

Contaminants may be accumulated by organisms (c) by direct injestion of suspended particulates, by passive sorption from solid surfaces and/or by consumption of contaminated food sources. Presence of contaminants in organisms clearly reflect the degree of bioavailability, although numerous factors (e.g. water chemistry, body weight and fat content, genetic composition, excretion rates) affect biouptake. Contaminants associated with sediments may be accumulated in the food web resulting in potentially adverse effects to high level consumers including man. Benthic-organisms directly transmit contaminants into the food web by injestion of suspended and bottom particulates (e.g. chironomids), predation on phytoplankton and zooplankton (e.g. shrimp), filter feeding (e.g. bivalves) and consuming detritus (e.g. snails). Fish consume particulates by direct exposure (sorption across gill surfaces) and bottom sediments by consumption of benthics; the latter route results in a higher level of accumulation. The problem with the hatching of herring gull eggs, first noted in the 1970's, is a well known example of biomagnification to a fish-eating, high trophic level of the food chain.

APPENDIX II.

ANALYTICAL METHODS AND MEASUREMENTS

A brief description of particle size and organic carbon analyses and of suspended sediment measurements and analysis are given.

II.1 Particle Size Analysis

Particle size analyses are performed on Water Resources Branch samples as part of the routine program. The Bottom Withdrawal tube method is most commonly used for suspended sediment samples. The method is effective for samples ranging in concentration from 300-10 000 mg/L and in size from 2-1 000µm, which include the Canadian range.

The Bottom Withdrawal tube method involves dispersing the sample in a glass tube with an outlet at the lower end. Draughts of known volume are drawn from the bottom at given time intervals, placed in evaporation dishes, oven dried and weighed. The sediment weight of each fraction is determined, and an Odén curve is constructed from data on the time taken for various size fractions to settle. Values interpreted from the curve are used to plot a particle size distribution curve (Water Resources Branch, 1984).

The minimum sample weight required for the analysis is 0.15g. It is current practice not to perform size analysis if sufficient

sediment is not retrieved in one sample container. If WRB is to provide routine size data for WQB using this analytical method, the possibility of collecting several samples to ensure that the minimum sediment weight is recovered should be considered.

The Bottom Withdrawal tube method produces satisfactory results for most samples. At concentration of 200 mg/L, the average error is about 5%. Higher concentrations (e.g. 1 000-3 000 mg/L) have less associated error (<3%). At concentrations of 5 000-10 000 mg/L, the error is reduced to about 1%. There is no definite change in accuracy of the method as sediment sizes vary, although more erratic results have been noted for the large sand fractions (Federal Inter-Agency River Basin Committee, 1953).

The method costs about $60/sample (1984/85 price).

II.2 Organic Carbon Content Analysis

Water Quality Branch laboratories determine the organic carbon content of sediment samples with a CHN Analyzer. The method is applicable for the determination of particulate organic carbon in waters in the range 1µg/L-100 mg/L, and can also be modified for analyses of carbon in sediments.

The sediment suspension is vacuum filtered through pretreated GF/C filters. The volume of water filtered depends on the sediment

concentration. As rough guidelines, about 500 mL of water sample should be filtered if the sediment concentration is 10 mg/L or more, one litre if the concentration is 5-10 mg/L. About 0.6 - 0.8 mg of sediment is required. The residue is washed with sulphuric acid to dissolve carbonates which, if not removed, may produce high organic carbon values. The filter paper and residue are dried in a dessicator then organic carbon content is determined in the Analyser with manganese dioxide (added as a catalyst) to oxidize carbonaceous material to carbon dioxide and water (Water Quality Branch, 1979).

The method costs about $10/sample (1984/85 price).

II.3 Suspended Sediment Measurement and Analysis

Water Resources Branch collects samples for determining suspended sediment concentration by depth-integrated and point-integrated sampling.

a) The depth integrated method is used to determine the sediment load and sediment concentration in a cross-section, where the depth is less than five metres. To take the measurement, the cross-section is divided into at least five equal-flow portions and a representative sample is collected from each portion. The sediment discharge for the cross-section is computed by adding the discharge-weighted concentrations of each portion.

b) The point-integrated method is used to compare with the depth-integrating method and to obtain samples for particle size analysis, where the depth is greater than five metres. The sediment discharges are computed by graphical methods.

The sediment concentration must be determined for two purposes: calculation of loadings at locations in the river system and for selection of an representative location in a river cross-section for collection of sediment-contaminant samples. In the former case WRB would provide the data as part of routine sampling. In the latter case, data on the cross-sectional variability and advice concerning a "representative" location at which to collect sediment samples would be needed by WQB. For example, a study of suspended sediment concentrations at two sites on prairie rivers revealed that sampling at a single vertical at any of several locations could yield an estimate of the average cross-sectional concentration within 4% (WRB, 1979). Site specific information of this type will be needed at all stations of WQB interest.

Determination of sediment concentration is carried out at WRB laboratories by (a) evaporation and b) filtration. In method (a), water is evaporated from the settled sediment sample; the results are corrected for dissolved solids. The method is used when a high proportion of fine material is present. In the filtration method (b), the sediment-water mixture is decanted and the remaining slurry is vacuum filtered and dried.

The evaporation and filtration methods cost $11 and $15 respectively (1984/85 price).